Indirect N2O emissions with seasonal variations from an agricultural drainage ditch mainly receiving interflow water

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Title: Indirect N_2O emissions with seasonal variations from an agricultural drainage ditch mainly receiving interflow water

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Abstract

Nitrogen (N)-enriched leaching water may act as a source of indirect N_2O emission when it is discharged to agricultural drainage ditches. In this study, indirect N_2O emissions from an agricultural drainage ditch mainly receiving interflow water were measured using the static chamber-gas chromatography technique during 2012−2015 in the central Sichuan Basin in southwestern China. We found the drainage ditch was a source of indirect N_2O emissions contributing an inter-annual mean flux of 6.56 ± 1.12 μg N m^{-2} h^{-1} and a mean indirect N_2O emission factor (EF_{5g}) value of 0.03 ± 0.003%. The mean EF_{5g} value from literature review was 0.51%, which was higher than the default EF_{5g} value (0.25%) proposed by the Intergovernmental Panel on Climate Change (IPCC) in 2006. Our study demonstrated that, more *in situ* observations of N_2O emissions as regards N leaching are required, to account for the large variation in EF_{5g} values and to improve the accuracy and confidence of the default EF_{5g} value. Indirect N_2O emissions varied with season, higher emissions occurred in summer and autumn. These seasonal variations were related to drainage water NO_3^--N concentration, temperature, and precipitation. Our results showed that intensive precipitation increased NO_3^--N concentrations and N_2O emissions, and when combined with warmer water temperatures, these may have increased the denitrification rate that led to the higher summer and autumn N_2O emissions in the studied agricultural drainage ditch.

Capsule: N_2O fluxes from the agricultural drainage ditch varied with season, and the mean indirect N_2O emission factor was 0.03 ± 0.003%.

Key words: Nitrous oxide (N_2O); Indirect N_2O emission factor (EF_{5g}); Intensive precipitation; Nitrate; Leaching; Drainage ditch

1. Introduction

Atmospheric concentrations of the ozone-depleting, and potent greenhouse gas nitrous oxide (N_2O), have increased from a pre-industrial level of 270 ppb to 324 ppb in 2011. One of the main causes of this rise in atmospheric N_2O is the increasing use of nitrogen (N) fertilizers (Ravishankara et al., 2009; IPCC, 2013). Considerable amounts of N are lost from N-fertilized agricultural land via leaching and runoff, and which is ultimately transported into groundwater, drainage ditches, rivers and estuaries, consequently causing N pollution in aquatic ecosystems (Mosier et al., 1998; Mulholland et al., 2008; Zhu et al., 2009; Gumiero et al., 2011). There have been several reports of groundwater contaminated with high nitrate (NO_3^-) concentrations in areas of high fertilizer use (Groffman et al., 1998; McMahon et al., 2000; Hiscock et al., 2003; Jahangir et al., 2013). In addition to studies on direct emissions of N_2O from N fertilized soils, indirect N_2O emissions from aquatic ecosystems that are associated with N leaching and runoff in agricultural areas deserve attention (Nevison, 2000; Beaulieu et al., 2008; Outram and Hiscock, 2012; Tian et al., 2017). The N-enriched groundwater associated with N leaching is considered a source of indirect N_2O emissions via denitrification or degassing when it is discharged to adjacent watercourses such as drainage ditches and streams (McMahon et al., 2000; Reay et al., 2004a and 2004b; Minamikawa et al., 2011; Jurado et al., 2017). Werner et al. (2012), for example, found that agricultural streams were a significant source of N_2O, while Jurado et al. (2017) also found that groundwater could act as a source of N_2O to the atmosphere and with the highest level of N_2O flux in springs supplied by groundwater

compared with those in wetland and estuarine areas. Reay et al. (2004a and 2004b) reported that concentrations of dissolved N_2O in leachate rapidly decreased on entry to drainage ditches.

Drainage ditches in farmlands are generally ubiquitous and, as such, represent important hydrologic conduits for surface and subsurface N flow to aquatic systems (Kröeger et al., 2007; Shen et al., 2016; Zhu et al., 2012). Many drainage ditches are polluted and suffer from eutrophication, owing to losses of N from agriculture (Janse and Van Puijenbroek, 1998). But drainage ditches also act as important sites for biogeochemical interactions between reactive N, aquatic plants, microorganisms, and the physical environment (Janse and Van Puijenbroek, 1998; Shen et al., 2016; Zhang et al., 2016). Consequently, drainage ditches have been identified as hotspots for N removal and N_2O emissions (Reay et al., 2003, 2004a; Kröeger et al., 2007; Zhang et al., 2016). It is possible that spatial and temporal variations in N_2O emissions can be caused by dynamic changes in drainage water NO_3^- concentrations and other geochemical and hydrological parameters (Beaulieu et al., 2009; Jurado et al., 2017; Tian et al., 2017). It has thus been suggested that these variations should be considered in improving the certainty of quantification of indirect N_2O emissions (Werner et al., 2012; Jurado et al., 2017).

The Intergovernmental Panel on Climate Change (IPCC) has defined the emission factor for indirect N_2O emissions from leaching and runoff from agricultural systems as EF_5. This EF_5 incorporates three components: EF_{5g}, EF_{5r} and EF_{5e}, which are the emission factors for groundwater and surface drainage, rivers, and estuaries, respectively (IPCC 2006). The default value of the EF_5 was defined as the proportion of N leaching and runoff converted to N_2O in these water bodies (IPCC 2006). However, the default value proposed by the IPCC to estimate N_2O emissions in

drainage ditches and groundwater resulting from leached N has a lack of certainty (Clough et al., 2007a; Beaulieu et al., 2008; Outram and Hiscock, 2012; Jahangir et al., 2013), since it has decreased from 2.5% in 1997 to 0.25% in 2006, based on studies from a limited number of countries (IPCC, 2006; Outram and Hiscock, 2012). In view of the large variation (0.002%−73%) in the values of EF_{5g} (Jurado et al., 2017), the default value requires improvement by increasing the number of global *in situ* observations (Reay et al., 2003; Beaulieu et al., 2008; Outram and Hiscock, 2012).

In China, the sloping farmland of the purple soils in the central Sichuan Basin is particularly vulnerable to N loss via NO_3^--N leaching due to a combination of intensive farming practices, hilly topography, climate, and soil characteristics (Zhu et al., 2009; Wang and Zhu, 2011; Gao et al., 2014), where the annual loss of N from these soils via interflow was reported to be 37.9 kg ha^{-1}, and accounted for 88% of the total N loss (Zhu et al., 2009). Interflow is the lateral movement of water in the unsaturated zone, that returns to the surface or enters a stream prior to becoming groundwater. Interflow was reported as an important water flow pattern in this area (Zhao et al., 2013), where the main N loss pathway from the local farmland is NO_3^--N leaching via interflow (Wang and Zhu et al., 2011). Previous studies have also reported that interflow was the predominant pathway of water discharge (Zhu et al., 2009; Zhao et al., 2013; Hua et al., 2014) and a primary source of water for shallow groundwater recharge, ditches, and streams in this area (Wang and Zhu et al., 2011; Zhao et al., 2013). This region is a nitrate sensitive area, because the loading of nitrate leaching in the purple soil area is more than 2-fold the average loss in China (Zhou et al., 2013; Zhang et al., 2013). There is severe NO_3^--N pollution of groundwater (mean concentration of NO_3^--N >10 mg L^{-1}) and water eutrophication in the region (Zhu et al., 2009; Wang and Zhu, 2011; Zhou et al., 2013). Moreover, the

120 long-distance movement of N discharged from the purple soil area may have a
121 profound impact on the water quality of the nearby Yangtze River (Wang and Zhu,
122 2011).

123 Indirect N_2O emissions from an agricultural drainage ditch mainly receiving
124 interflow were measured for three years *in situ* in southwestern China in this study.
125 The objectives of this study were to quantify the indirect N_2O emissions from
126 agricultural drainage ditches, examine the temporal variation in N_2O emissions, and
127 explore the factors affecting the indirect N_2O emissions, since little is known about
128 the indirect N_2O emissions and EF_{5g} from drainage ditches mainly receiving interflow
129 water in this area.

130

131 **2. Materials and Methods**

132 *2.1. Study area*

133 The field study was carried out at the Yanting Agro-Ecological Station of Purple
134 Soil (N 31°16', E 105°28'), a station of the Chinese Ecosystem Research Network
135 (CERN), Chinese Academy of Sciences (CAS), in an important agricultural area in
136 the upper tributary of the Yangtze River Watershed (Figs. 1a and 1b). Altitude at the
137 study area ranges between 400 and 600 m, and the surface is mainly covered by low
138 mountains, and hills. The area has a humid subtropical monsoon climate, with an
139 annual (1981−2009) mean temperature of 17.3°C and seasonally variable precipitation
140 of 836 mm spring: 5.9%; summer: 65.5%; autumn: 19.7%; and, winter: 8.9%; from
141 1981 to 2006 data, after Zhu et al. (2009).

142 The drainage ditches were located in the valley bottom of a small agricultural
143 catchment (0.15 km^2; Fig. 1b) of the first-order tributary of the Yangtze River (Zhu et
144 al., 2012), where the land use was dominated by sloping farmland of purple soil and
145 forest. The soil is classified as a Regosol (FAO Soil Taxonomy) or a

Pup-Orthic-Entisol (Chinese Soil Taxonomy) (Zhu et al., 2012). Land use distribution reflected the topography, with paddy fields on low-lying parts of hills, and farmland on slopes ranging from 3° to 15°. Forestry is mainly concentrated on upper parts of the hills. Rice (*Oryza sativa* L.) is cultivated in the paddies in the rainy season (from the middle of May to September) with applications of 150 kg N ha^{-1}, while oilseed rape (*Brassica napus* L.) is cultivated in the dry season (from late October to early May) with an application of 130 kg N ha^{-1} in late October. Maize (*Zea mays* L.) is planted on sloping farmland in the rainy season and winter wheat (*T. aestivum* L.) is cultivated in the dry season, with applications of 150 kg N ha^{-1} and 130 kg N ha^{-1}, respectively. Forestry is dominated by Alder, *Alnus cremastogyne* Burk., and Cypress (*Cupressus funebris* Endl) plantations. The drainage ditch was surrounded by the upland farmlands, vegetable fields and paddy rice fields (Fig. 1b). The width and depth of the drainage ditch was ~70 cm and 70−100 cm, respectively. The water depth in the ditch, measured using a stainless steel ruler, was shallow (0.6−6.4 cm) with a slow velocity during the observation period, and with sediment depth < 20 cm. The ditch was artificially excavated, and the purplish shale and soil layer interface was exposed to help leaching water laterally flow into the drainage ditch, since the bedrock has extremely weak permeability (Zhu et al., 2009; Zhao et al., 2013; Fig. 1c). Moreover, the local groundwater level is usually very shallow (-45.5−-193.2 cm, Zhang et al., 2017), and the ditch receives shallow groundwater recharge and leaching water for most of the year, while it also receives overland flow for a short period of time (1−2 days) after intensive precipitation. Thus, this drainage ditch receives interflow as the main water source. During the early spring (dry season), there is no water in the drainage ditch for several days. Vegetation in the study ditch mainly comprised *Lolium perenne* L., *Echinochloa crus-galli* (L.) Beauv., *Fimbristylis*

171 *milliacea* (L.) Vahl, *Polygonum hydropiper*, and other ruderal weeds.

172

173 *2.2. Sample collection and analysis*

174 The N_2O emissions from drainage ditch were measured *in situ* by employing the
175 static chamber-gas chromatography technique. However, this technique may cause
176 artefacts in determining N_2O emission due to the effect of water turbulence around
177 the chamber (Clough et al., 2011). Nonetheless, the floating chamber method could be
178 relatively simple and rapid methodology for observation of representative N_2O
179 emissions from rivers (Xia et al., 2014), and the N_2O fluxes measured by floating
180 chamber might be slightly higher than those calculated from N_2O concentration data
181 (Harrison et al., 2003). However, the water depth of the drainage ditch in the present
182 study was quite shallow and unsuitable for using the floating chamber method to
183 measure N_2O emission flux. Thus the static chamber technique was used in this study,
184 where four chambers were installed at 25−30 m intervals around the interflow
185 discharge outlet spanning a length of 100 m. The chambers contained two parts: a
186 chamber cover measuring 50 cm × 50 cm × 50 cm as a five-plane cube, and a square
187 base collar measuring 50 cm long × 50 cm wide × 10 cm high with a 3 cm × 3 cm
188 groove on the top. The materials and structures of the two parts of chambers were
189 previously reported (Tian et al., 2017). The base collars were inserted into the ditch
190 sediment at a depth of ~10 cm (Fig. 1d), and kept in place for the one-year
191 observation period, before they were moved to near the original sampling point in the
192 following year. There were some holes (Φ 2.0 cm) equally distributed in the side walls
193 of the base collar to allow the lateral transfer of water plants, animals and microbes,
194 and sediment nutrients (Tian et al., 2017). When gases were sampled, the chamber
195 covers were temporarily placed onto the base collar and the holes in the side walls of

196 the base collars were submerged in drainage water to avoid gas leakage. Gas samples
197 were collected between 9:00−11:00 am, 1−2 times per week from 1st December to 30th
198 November in 2012−2013, 2013−2014, and 2014−2015. On each sampling occasion,
199 five × 50 mL of chamber air were collected at 0, 7, 14, 21, and 28 min after closing
200 the chamber, using a plastic syringe mounted with a three-way valve. The sample
201 N_2O concentrations were measured within 24 hours after gas collection, using a gas
202 chromatograph (Agilent 7890, Santa Clara, CA, USA) fitted with an electron capture
203 detector (ECD) that was operated at 330°C. The depth of water and water temperature
204 (WT) at 0−5 cm depth, air temperature in the chamber and pH (in 2014–2015 only)
205 were recorded concurrently with gas emission sampling. The water dissolved oxygen
206 (DO) concentrations in the ditch were only measured *in situ* during the second half of
207 the third observation year, because of the late arrival of purchased instrument for
208 measuring DO. In 2013–2014 and 2014–2015, 500 mL of water was collected from
209 each gas emissions recording site and transported in an insulated box filled with
210 ice-packs to the laboratory, where the samples were stored at 4°C until analysis for
211 inorganic N and dissolved organic carbon (DOC) concentrations using methods
212 reported by Tian et al. (2017). Meteorological data (daily precipitation, air
213 temperature and barometric pressure) were obtained from the meteorological station
214 at the Yanting Agro-Ecological Station of Purple Soil of CERN, located
215 approximately 1 km away from the study site.
216
217 *2.3. Data analysis*
218 The N_2O fluxes (μg N m^{-2} h^{-1}) were calculated from the increases in N_2O
219 concentrations of the five gas samples within the measurement period (Tian et al.,
220 2017). The cumulative N_2O emissions (kg N ha^{-1}) were derived from the flux

calculations using a linear interpolation method (Zhou et al., 2013, 2015; Tian et al., 2017). Although linear interpolation method is commonly used in previous studies, it has some uncertainties in estimating N_2O emission, because this method might miss short-lived N_2O emission peaks, given the episodic nature of indirect N_2O fluxes. We calculated the EF_{5g} value from the mass ratio of emitted N_2O-N to NO_3^--N in a unit volume of drainage water (Well et al., 2005b; IPCC, 2006). We averaged all EF_{5g} in each observation season and annual year for the mean values of seasonal and annual EF_{5g}.

In our study area, winter starts from December to the end of February, summer includes June, July and August, spring and autumn are during the transitions between winter and summer. The inter-annual and seasonal variations in N_2O emissions and mean values of drainage water variables were assessed using one-way ANOVA, followed by Hochberg's GT2 multiple comparison test ($P < 0.05$). Using simple linear regression, we tested for relationships between drainage water NO_3^--N concentration and the accumulated amount of intensive rainfall (> 15 mm) that fell 3 days prior to measuring water variables, cumulative N_2O emissions and accumulated rainfall during each rainfall event, and drainage water NO_3^--N concentration following each rainfall event in 2014–2015. Only the accumulated amount of precipitation > 15 mm were used for the analysis, i.e., when the drainage water NO_3^--N concentration was measured on 24th May, the accumulated precipitation 3 days prior to measuring NO_3^--N was cumulative rainfall from 21th to 22th May. Emission of N_2O during each rainfall event defined as cumulative N_2O emission during the rainy days and subsequent 2 days for probable N leaching, i.e., when 21th to 22th May were rainy days, the period for cumulative N_2O emission was from 21th May to 24th May. The relationships between ln (mean seasonal N_2O flux) and seasonal precipitation, mean

seasonal air and water temperature were also analyzed using simple linear regression analysis, which was also used for those relationships analysis on monthly scale. Data for monthly and seasonal N_2O fluxes were ln transformed and statistical analyses were performed using SPSS version 20.0 (SPSS, Inc., USA).

3. Results

3.1. Temperature and precipitation

Mean daily air temperature ranged from 0.4 to 30.6°C during the experimental period, 2012–2015, where mean annual air temperature was 17.3, 16.6, and 17.0°C in 2012–2013, 2013–2014 and 2014–2015, respectively (Fig. S1a). Mean seasonal air temperature was 6.63, 17.9, 25.8 and 17.3°C, in winter, spring, summer, and autumn, respectively. Water temperature ranged from 3.4 to 27.4°C during the three year study period, where mean annual temperature was 17.0, 15.3, and 17.6°C in 2012–2013, 2013–2014, and 2014–2015, respectively (Fig. S1b). There were seasonal variations in mean water temperature, where it was 7.1, 15.0, 23.7, and 20.7°C in winter, spring, summer, and autumn, respectively. There was a positive correlation between water temperature and air temperature ($r = 0.97$, $n = 131$).

Annual precipitation was 1272, 821, and 956 mm in 2012–2013, 2013–2014, and 2014–2015, respectively (Fig. S1c). The mean seasonal precipitation in winter, spring, summer, and autumn was 18.2, 147, 519, and 333 mm, respectively, where 83.8% of the precipitation occurred in summer and autumn.

3.2. Drainage water

Depth of the drainage ditch water varied from 0.6 cm to 6.4 cm (mean: 1.8 cm), with higher mean seasonal water depths in summer and autumn than those in winter

and spring (data not shown). We recorded pH of the water during 2014–2015 and found the mean was 7.56, with no variation among the seasons, and similarly, there was no seasonal variation in NH_4^+-N concentrations (Table 1). Concentrations of NH_4^+-N (range: 0.03–0.31 mg N L^{-1}, mean: 0.11 mg N L^{-1}) were lower ($P < 0.001$) than those of NO_3^--N (range: 0.20–17.0 mg N L^{-1}, mean: 3.75 mg N L^{-1}; Fig. 2a). The mean NO_3^--N concentration in autumn was higher ($P < 0.05$) than those in the other seasons in 2013–2014 and 2014–2015 (Table 1). However, neither concentration of NH_4^+-N nor NO_3^--N varied between 2013–2014 and 2014–2015 ($P > 0.05$; Table 1). Concentrations of DOC ranged from 0.49 to 6.28 mg C L^{-1}, and had a mean value of 2.25 mg C L^{-1} (Table 1; Fig. 2b).

3.3. Indirect N_2O emissions and N_2O emission factor (EF_{5g})

Over the three years, N_2O fluxes ranged from -0.33 to 40.3 μg N m^{-2} h^{-1} (Fig. 3), with a mean of 6.56 μg N m^{-2} h^{-1} and a cumulative emission of 1.38 kg N ha^{-1} (Table 1). Mean annual N_2O fluxes were 4.72, 5.20, and 9.77 μg N m^{-2} h^{-1} in 2012–2013, 2013–2014, and 2014–2015, respectively (Table 1), and there were no variations in mean annual fluxes or total annual N_2O emissions (Table 1). But the cumulative seasonal N_2O emissions in winter in 2014–2015 were higher than those in winter in 2012–2013 and 2013–2014 (Fig. 4). We also found within-year seasonal differences in each of the three years, where cumulative seasonal N_2O emissions were higher in summer than in spring in 2012–2013 ($P < 0.05$), higher in summer and autumn than in winter and spring in 2013–2014 ($P < 0.05$), and higher in summer and autumn than in spring in 2014–2015 ($P < 0.05$; Fig. 4).

We found that the EF_{5g} values ranged from 0.002% to 0.19%, with a mean of 0.03%, with no variation in value between 2013–2014 and 2014–2015 (Table 1).

296 However, mean EF_{5g} in summer was higher ($P < 0.05$) than those in the other seasons
297 in 2013–2014 (Table 1).
298
299 *3.4. Relationships between N_2O dynamics and environmental factors*
300 There were positive relationships between the cumulative precipitation (> 15 mm)
301 3 days prior to measuring NO_3^--N and drainage water NO_3^--N concentration
302 measured after precipitation in 2014–2015 ($R^2 = 0.55$, $P < 0.05$, $n = 12$; Fig. 5a), the
303 cumulative precipitation and the cumulative N_2O emissions during rainfall events (R^2
304 = 0.35, $P < 0.05$, $n = 13$; Fig. 5b), and cumulative N_2O emissions during rainfall
305 events and drainage water NO_3^--N concentration measured after rainfall events (R^2 =
306 0.55, $P < 0.05$, $n = 12$; Fig. 5c). There were positive relationships between ln (mean
307 monthly N_2O flux) and mean monthly air temperature ($R^2 = 0.36$, $P < 0.001$, $n = 33$;
308 Fig. 6a), mean monthly water temperature ($R^2 = 0.47$, $P < 0.001$, $n = 33$; Fig. 6b), and
309 monthly cumulative precipitation ($R^2 = 0.24$, $P < 0.05$, $n = 33$; Fig. 6c). We also found
310 positive relationships between ln (mean seasonal N_2O flux) and mean seasonal air
311 temperature ($R^2 = 0.46$, $P < 0.05$, $n = 12$; Fig. 6d), mean seasonal water temperature
312 ($R^2 = 0.35$, $P < 0.05$, $n = 12$; Fig. 6e), and seasonal cumulative precipitation ($R^2 = 0.53$,
313 $P < 0.05$, $n = 12$; Fig. 6f).
314
315 **4. Discussion**
316 *4.1. Comparison with other studies*
317 When we compared this study with previous studies on indirect N_2O fluxes from
318 groundwater and drainage water (Table 2), we found our result (6.56 μg N m^{-2} h^{-1})
319 was higher than those from the UK (Aberdeenshire, Reay et al., 2009; Cambridgeshire,
320 Mühlherr & Hiscock, 1997, and Hiscock et al., 2003; Norfolk, Hiscock et al., 2003,

and Hama-Aziz et al., 2017), the USA (the High Plains aquifer, McMahon et al., 2000), and France (the Seine Basin, Vilain et al., 2012), but similar to fluxes from drainage water in Japan and Canada (Table 2). But, the value in this study was much lower than those ranging between 35.2 and 7440 μg N m^{-2} h^{-1} recorded from the UK (Midlothian, Reay et al., 2003 and Norfolk, Outram and Hiscock, 2012), the USA (the Kalamazoo River Basin, Beaulieu et al., 2008; the Choptank River and Nanticoke River Basins, Gardner et al., 2016), Italy, and Sweden (Table 2). We also found that, the mean N_2O flux was similar to direct N_2O fluxes (7.53 μg N m^{-2} h^{-1}) from a rice-rapeseed rotation without N fertilization located in the same study area (Zhou et al. 2015). We deduce, therefore, the agricultural drainage ditches mainly receive interflow water represent non-negligible sources of indirect N_2O emission in the central Sichuan Basin in China.

We summarized the EF_{5g} values from peer-reviewed papers reported before 2017 (Table 2), and found the mean indirect N_2O emission factor (EF_{5g} = 0.03%) in the current study was at the lower end of the range (0.01%–4.76%), although the reason for the relatively low EF_{5g} value in our study was not clear. The mean EF_{5g} (0.51%) from the literature (median: 0.18%, 95% confidence interval: 0.24%, n = 70) was higher than the default value (0.25%) proposed by the IPCC in 2006. Although the number of studies on EF_{5g} has increased since publication of the 2006 IPCC guidelines, studies on these indirect N_2O emissions remain limited (Clough et al. 2007a), and there is uncertainty about the validity of the default EF_{5g} values and the application of a single value to all drainage waters and groundwaters, due to highly variable EF_{5g} values at regional and global scales (Jurado et al., 2017; Table 2). We suggest, more *in situ* observations of indirect N_2O emission and EF_{5g} are needed to improve the reliability and confidence in the use of EF_{5g}.

346

347 *4.2. Seasonal variations of N_2O emissions and affecting factors*

348 The increase of intensive rainfall amount resulted in an increase in the level of
349 NO_3^--N in the drainage ditch mainly receiving interflow water (Figs. 2a and 5a),
350 confirming that rainfall affects N leaching and NO_3^--N pollution in subsurface runoff
351 in this study area (Zhu et al., 2009; Wang and Zhu, 2011). In addition, the mean N_2O
352 fluxes increased with cumulative monthly and seasonal precipitation (Figs. 6c and 6f).
353 Our results suggest that seasonal precipitation patterns contribute to seasonal
354 variations in NO_3^--N levels and N_2O fluxes in drainage ditches mainly receiving
355 interflow water, which is consistent with the relationships of seasonal distributions of
356 precipitation and the seasonal variations in NO_3^--N and N_2O emissions that have been
357 reported from other agricultural headwater streams (Royer et al., 2006; Beaulieu et al.,
358 2009).

359 In our study, the drainage ditch water was rich in NO_3^--N and DOC, and may
360 have contained sufficient substrates for the occurrence and stimulation of
361 denitrification (Stow, et al., 2005; Beaulieu et al., 2009; Werner et al., 2012; Jahangir
362 et al., 2013). Our results showed that the concentration of DOC in the drainage water
363 was relatively high (Table 1) and was not related to N_2O emissions, indicating that
364 DOC was not a limiting factor for seasonal variations in N_2O emissions. However, the
365 concentration of NO_3^--N in the drainage water showed a positive relationship with the
366 N_2O emission (Fig 5c), which was similar to findings that both denitrification and
367 N_2O production rates increase with changes in groundwater chemical characteristics,
368 such as increasing the water NO_3^--N concentrations (Herrman et al., 2008; Beaulieu
369 et al., 2009, 2011; Jahangir et al., 2013; Jurado et al., 2017). Denitrification has been
370 shown to be active in generating N_2O in groundwater or areas rich in organic matter
371 where groundwater occurred (Koba et al., 2009; Jurado et al., 2017). The studied

drainage ditch was similarly rich in organic matter (7.43 g kg^{-1} soil) and DOC (mean: 41.2 mg kg^{-1} soil, range: 19.0–93.0 mg kg^{-1} soil). In addition, the DO concentration of the ditch water during the second half of the third observation year (5.58–8.57 mg L^{-1}, data not shown) was lower compared with that (7.5–15.5 mg L^{-1}) reported by Clough et al (2007b), where coupled nitrification–denitrification could occur; moreover, the main form of inorganic N was NO_3^--N rather than NH_4^+-N in the present study, which incurred that nitrification was much less likely to occur under this condition. Therefore, we suggest that the NO_3^--N concentration was a primary factor affecting N_2O fluxes produced via denitrification, which may explain the coherence of the seasonal changes in NO_3^--N concentrations and N_2O fluxes.

Our data also revealed a positive relationship between monthly and seasonal N_2O emissions and air and water temperature (Figs 6a, 6b, 6d, and 6e). Higher temperatures induce more rapid rates of metabolism for denitrifying bacteria (Herrman et al., 2008; Jurado et al., 2017), and Stow et al. (2005) and Tian et al. (2017) found N_2O fluxes increased with increasing water temperature in downstream rivers. Moreover, increased temperature can lower the amount of dissolved N_2O in the water which in turn promotes N_2O emissions, and reduce the DO concentration leading to anaerobic conditions thus promoting denitrification (Harrison et al., 2005; Clough et al., 2007b, 2011). Besides, significant diel changes in water temperatures and day-night oxygen fluctuations could also impact N transfer such as denitrification and N_2O production (Harrison et al., 2005; Clough et al., 2007b), although diel change was not measured in this study.

Our results further confirmed that indirect emissions were evidently sensitive to fluctuations of temperature and precipitation (Griffis et al., 2017). It is likely, therefore, that heavy precipitation increased leaching and associated higher NO_3^--N

concentrations in the drainage water, that when combined with warmer temperatures, resulted in stimulated denitrification and higher N_2O fluxes in summer and autumn.

Besides, we found a lack of inter-annual variation in indirect N_2O emissions, which may have been related to the lack of variation in DOC and inorganic N concentrations in the drainage ditch (Table 1), as a result of consistent annual mean temperatures, and management practices of the adjacent farmlands among the three study years. In contrast, some studies such as those in the US Corn Belt (e.g. Griffis et al., 2017) found inter-annual variations in indirect emissions attributed to warmer & wetter conditions. In the present study, 2012-2013 observation year was wetter than the other two years (precipitation: 1272 mm *vs.* 821 and 956 mm; Section 3.1), which might affect surface runoff and groundwater (Zhu et al., 2009; Wang and Zhu, 2011; Griffis et al., 2017). Wang and Zhu (2011) found that the annual mean leaching NO_3^--N concentration from local sloping farmland could be significantly lower in the wetter year (e.g. precipitation in 2006: 860 mm) than those in dryer years (e.g. precipitation in 2004: 806 mm). Although NO_3^--N concentrations of the ditch were not measured for the first observation year (2012-2013), high precipitation might lead to lower leaching NO_3^--N concentration in the first year. However, higher precipitation did not affect indirect N_2O emissions of the first year. The integrated influences of accumulated precipitation, water chemistry, and temperature could result in the N_2O emissions to be stable between years but vary with season in the drainage ditch during study period.

5. Conclusions

Large uncertainty still remains with respect to indirect N_2O emissions from agricultural systems, particularly from intensively managed farmlands such as those in

422 China. In the present study, we investigated indirect N_2O emissions from an
423 agricultural drainage ditch mainly receiving interflow water discharge in an intensive
424 farming area with high N inputs located in the central Sichuan Basin. The agricultural
425 ditch was a source of indirect N_2O emissions, with an inter-annual mean N_2O flux of
426 6.56 μg N m^{-2} h^{-1} and a mean EF_{5g} value of 0.03%. A review of the literature
427 revealed that the global average value of EF_{5g} was 0.51%. Although EF_{5g} in the
428 studied ditch was lower than the global average, it is not clear that the average figure
429 of intensive farming area in China is actually lower than the global average, because
430 only one previous study on EF_{5g} was available in China. Further field measurements
431 of EF_5 to reduce uncertainty in the estimate of EF_5 are needed. There were no
432 inter-annual variations in N_2O emissions, but there were seasonal differences, where
433 emissions were higher in summer and autumn than in winter and spring. In this study,
434 the seasonal variations were mainly related to seasonal dynamics of the drainage
435 water NO_3^--N concentration, temperature, and precipitation indicating the combined
436 effects of the interactions between these factors on these indirect N_2O emissions
437 should be considered. Our results suggest that intensive precipitation events increase
438 water NO_3^--N concentrations and stimulate N_2O emissions from drainage ditches
439 mainly receiving interflow water discharge. Moreover, the higher NO_3^--N
440 concentrations of the drainage water, when combined with warmer water temperature
441 in summer and autumn, may have stimulated denitrification and higher seasonal N_2O
442 emissions.
443
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691 **Figures captions**

692 **Fig. 1. (a)** Location and **(b)** catchment of the study site in southwestern China; **(c)**
693 profile of purple soil (left) and schematic illustration of post-rainfall water flow
694 movement in the study site purple soil type (right); and **(d)** schematic diagram of the
695 gas collection device in the field.

696

697 **Fig. 2.** Concentrations of NH_4^+, NO_3^- and DOC in drainage water during two years of
698 the study. Data points are means and error bars are the standard errors of replicates (*n*
699 = 4).

700

701 **Fig. 3.** N_2O fluxes recorded throughout the study period. Data points are means and
702 error bars are the standard errors of replicates ($n = 4$).

703

704 **Fig. 4.** N_2O emissions in each season over the three years study period. Data points
705 are means and error bars are the standard errors of replicates ($n = 4$). Different capital
706 letters indicate differences among the years, while different lowercase letters indicate
707 differences among the seasons ($P < 0.05$).

708

709 **Fig. 5.** Regression analyses of **(a)** accumulated amount of precipitation (> 15 mm)
710 that fell over the 3 days prior to measuring NO_3^--N and drainage water NO_3^--N
711 concentration following precipitation events; **(b)** N_2O emissions and accumulated
712 amount of precipitation during rainfall events; **(c)** N_2O emissions during each rainfall
713 event and drainage water NO_3^--N concentration after rainfall events.

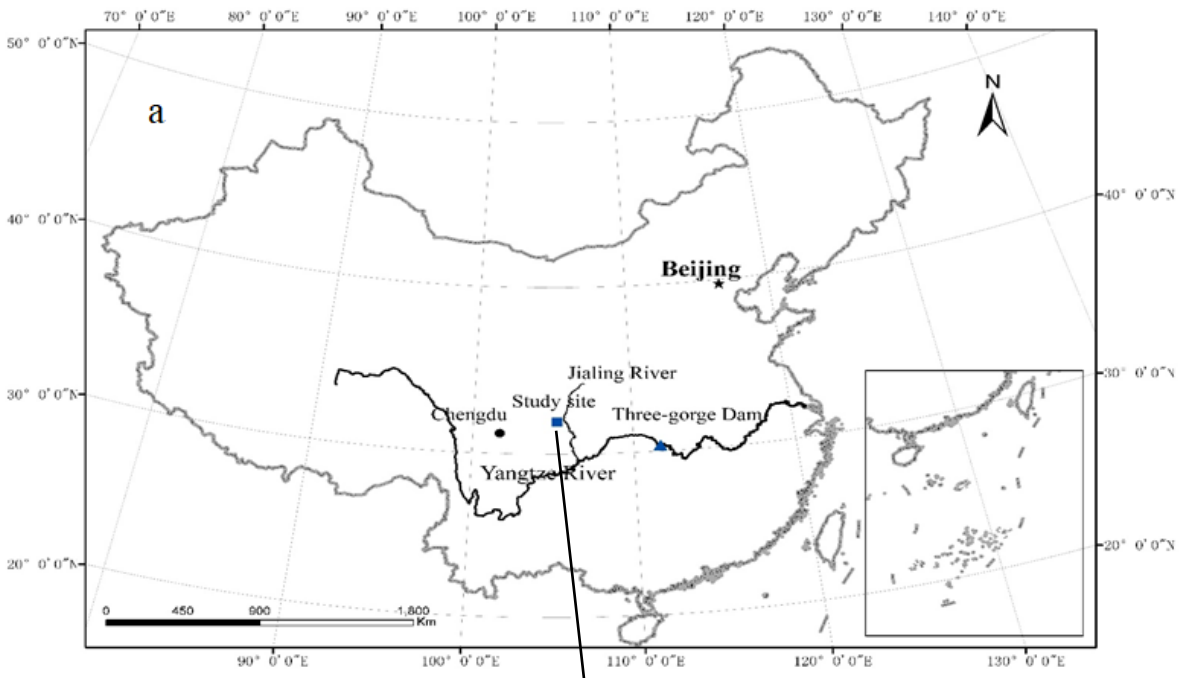
714

715 **Fig. 6.** Regression analyses of ln (mean monthly N_2O flux) and **(a)** mean monthly air
716 temperature; and **(b)** mean monthly water temperature; and **(c)** monthly precipitation,

and ln (mean seasonal N_2O flux) and **(d)** mean seasonal air temperature; and **(e)** mean seasonal water temperature; and **(f)** seasonal precipitation. Dashed lines are 95% confidence intervals.

720 **Fig. 1**

721



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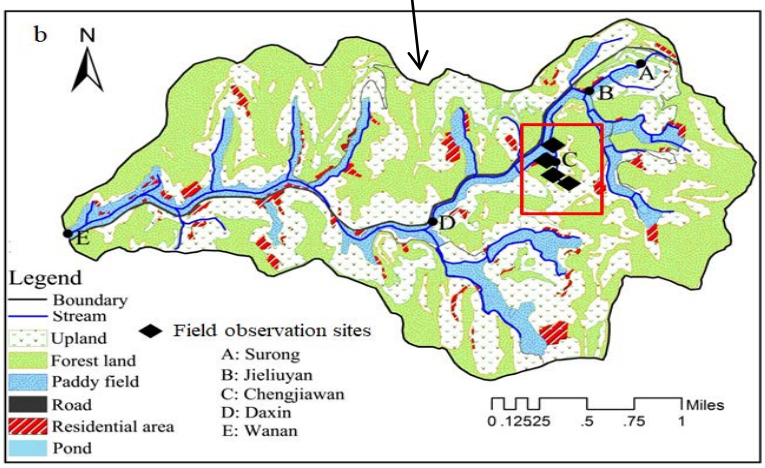

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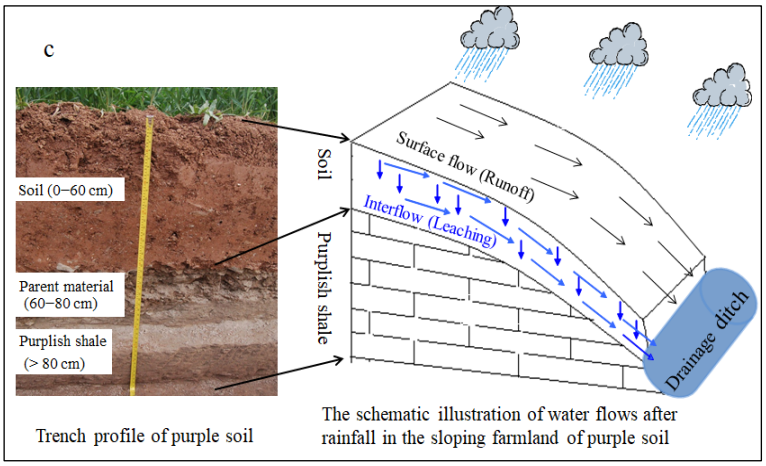
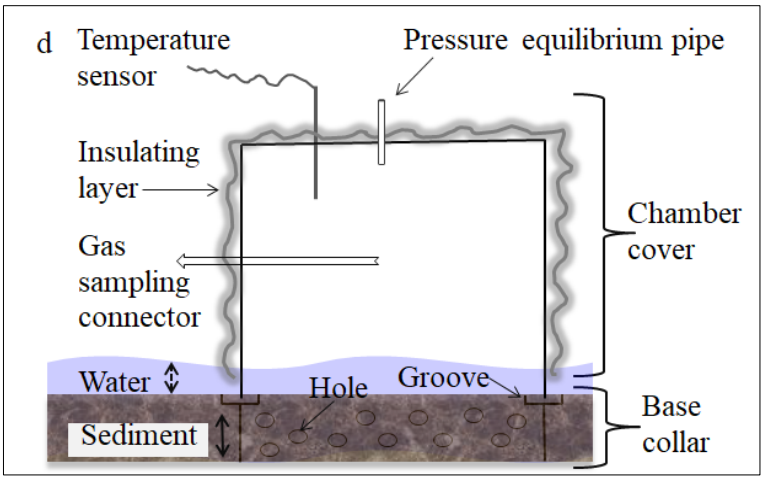
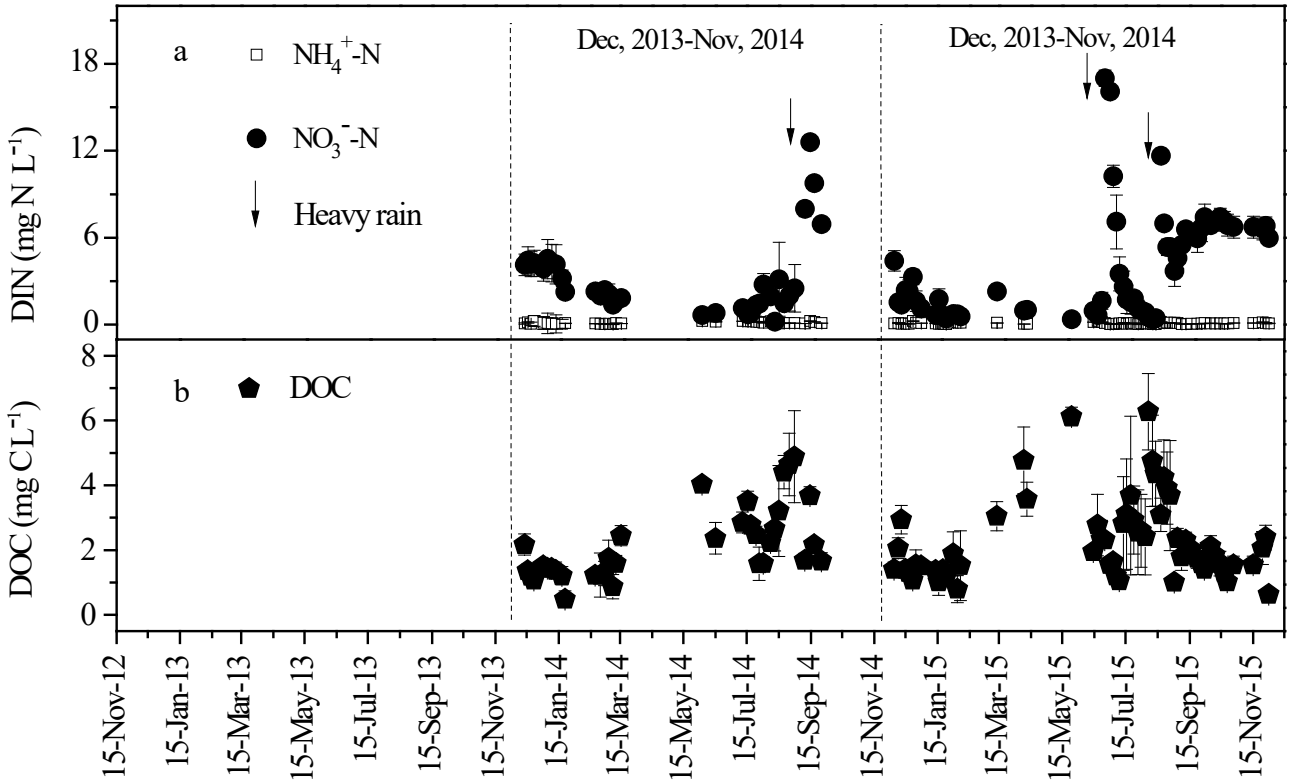


724

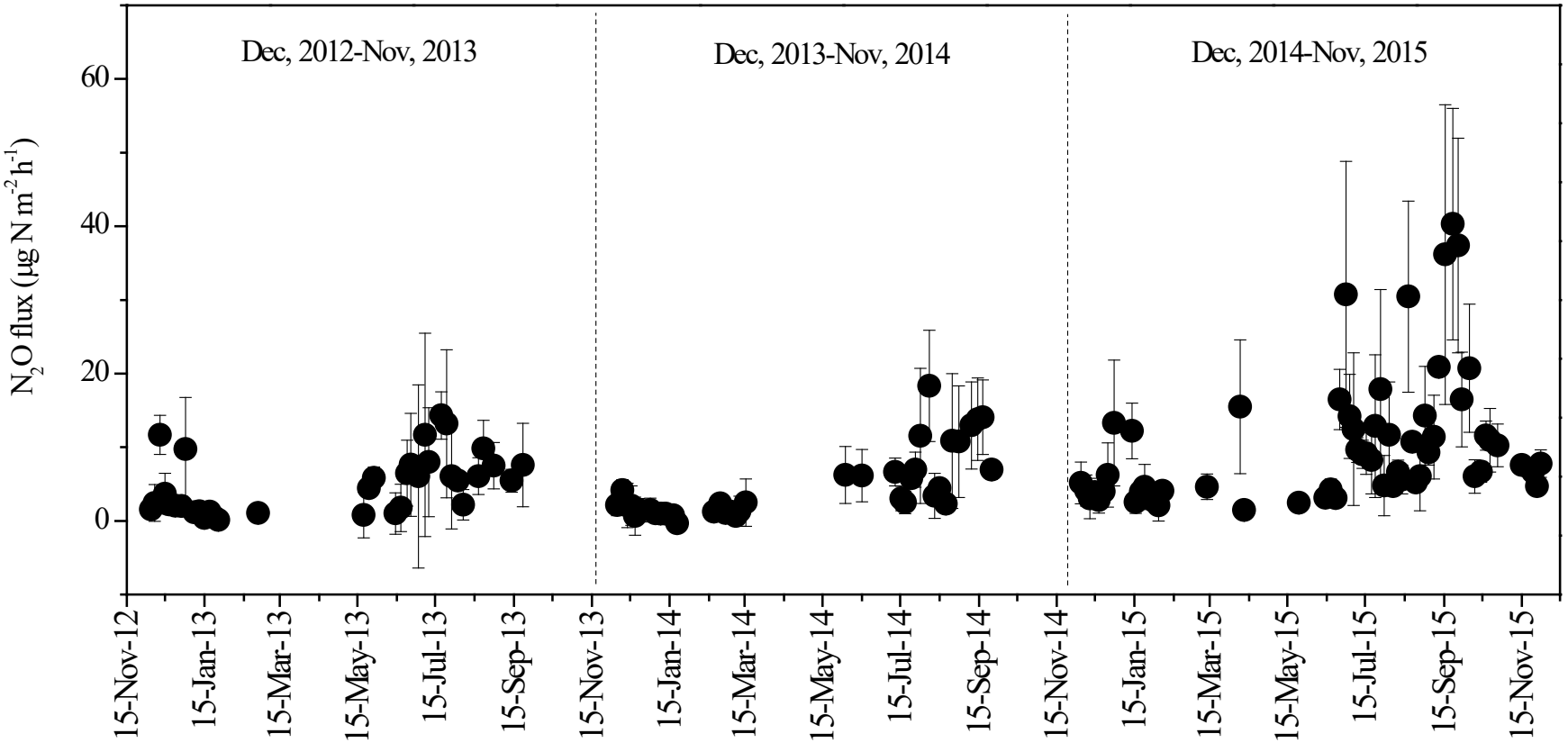

d
Temperature sensor
Pressure equilibrium pipe
Insulating layer
Gas sampling connector
Chamber cover
Water
Hole
Groove
Sediment
Base collar

725 **Fig. 2**


a
NH_4^+-N
NO_3^--N
Heavy rain
Dec, 2013-Nov, 2014
Dec, 2013-Nov, 2014
DIN (mg N L^{-1})
b
DOC
DOC (mg C L^{-1})
15-Nov-12
15-Jan-13
15-Mar-13
15-May-13
15-Jul-13
15-Sep-13
15-Nov-13
15-Jan-14
15-Mar-14
15-May-14
15-Jul-14
15-Sep-14
15-Nov-14
15-Jan-15
15-Mar-15
15-May-15
15-Jul-15
15-Sep-15
15-Nov-15

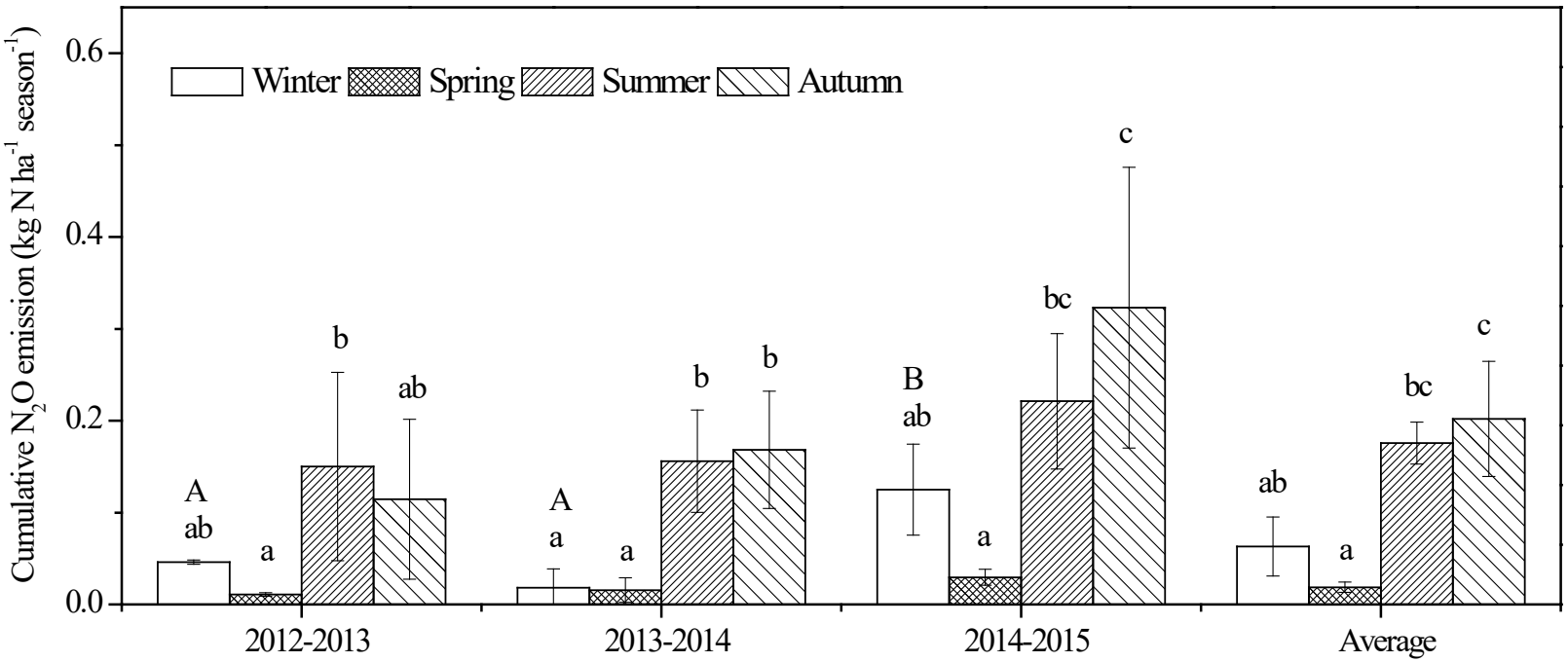
726

727 **Fig. 3**


Dec, 2012-Nov, 2013
Dec, 2013-Nov, 2014
Dec, 2014-Nov, 2015
N_2O flux ($\mu g\ N\ m^{-2}\ h^{-1}$)
60
40
20
0
15-Nov-12
15-Jan-13
15-Mar-13
15-May-13
15-Jul-13
15-Sep-13
15-Nov-13
15-Jan-14
15-Mar-14
15-May-14
15-Jul-14
15-Sep-14
15-Nov-14
15-Jan-15
15-Mar-15
15-May-15
15-Jul-15
15-Sep-15
15-Nov-15

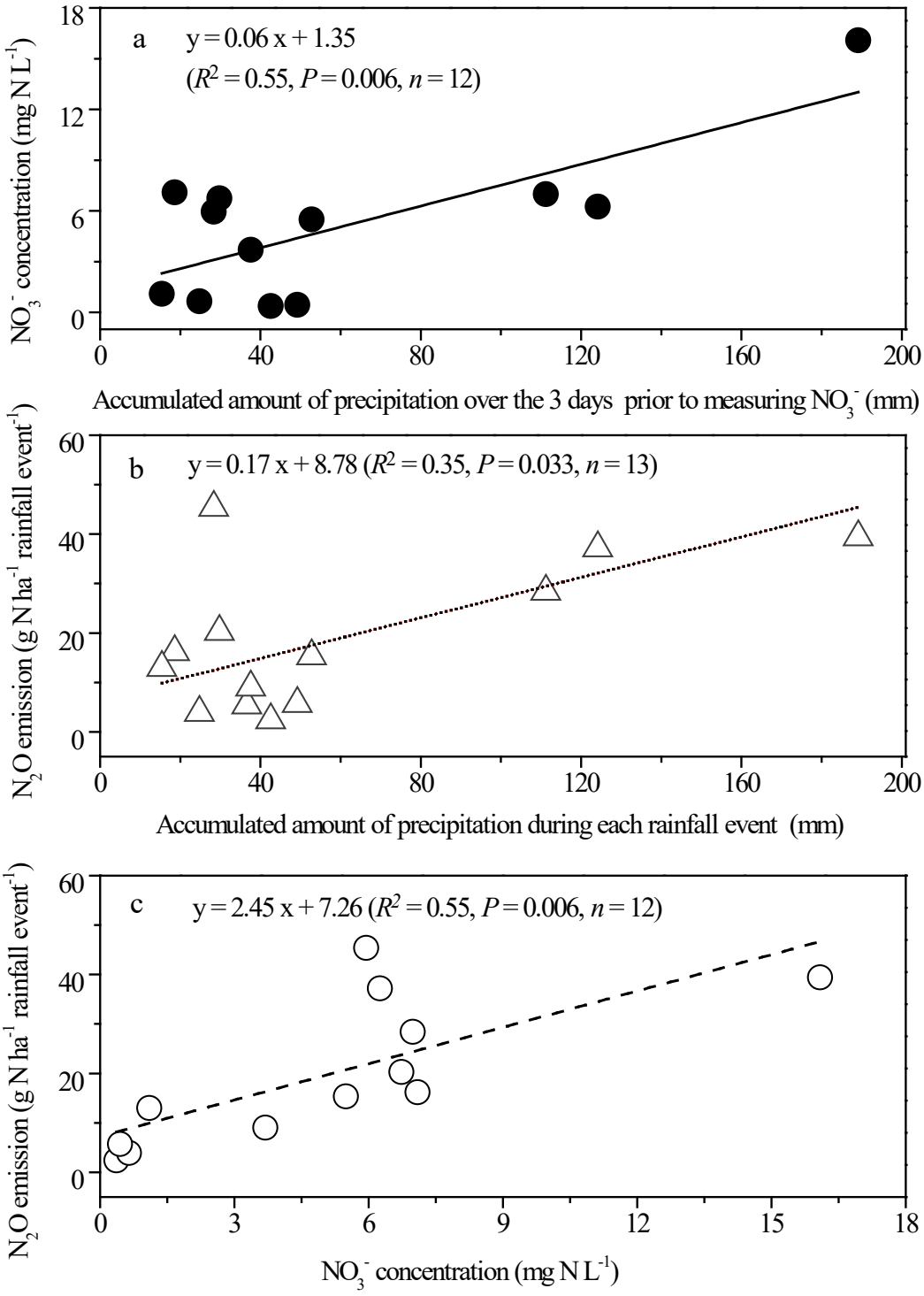
728

729 **Fig. 4**


Winter
Spring
Summer
Autumn
Cumulative N_2O emission (kg N ha^{-1} $season^{-1}$)
0.0
0.2
0.4
0.6
A
ab
a
b
ab
A
a
a
b
b
B
ab
a
bc
c
ab
a
bc
c
2012-2013
2013-2014
2014-2015
Average

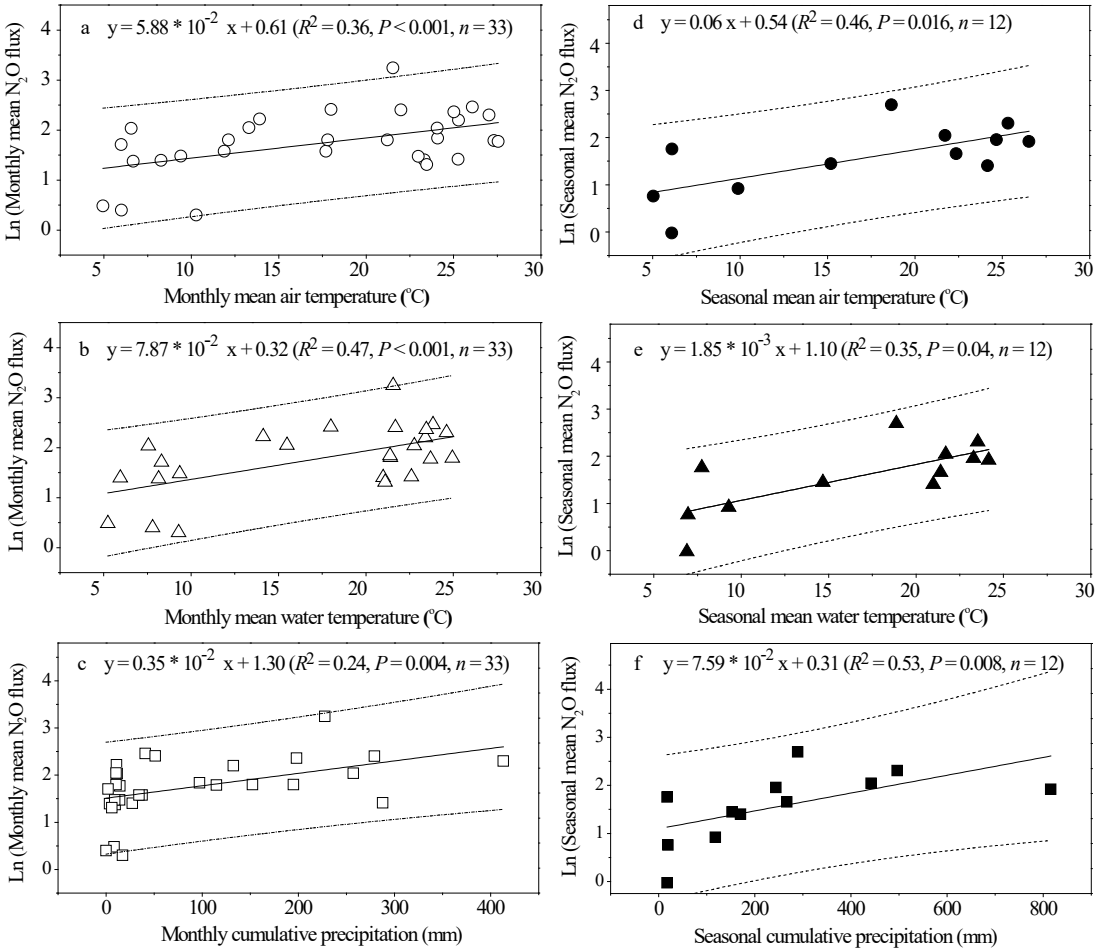
730

731 **Fig. 5**


a
y = 0.06 x + 1.35
(R^2 = 0.55, P = 0.006, n = 12)
NO_3^- concentration (mg N L^{-1})
Accumulated amount of precipitation over the 3 days prior to measuring NO_3^- (mm)
b
y = 0.17 x + 8.78 (R^2 = 0.35, P = 0.033, n = 13)
N_2O emission (g N ha^{-1} rainfall $event^{-1}$)
Accumulated amount of precipitation during each rainfall event (mm)
c
y = 2.45 x + 7.26 (R^2 = 0.55, P = 0.006, n = 12)
N_2O emission (g N ha^{-1} rainfall $event^{-1}$)
NO_3^- concentration (mg N L^{-1})

732

733 **Fig. 6**



734
735

Table 1 Seasonal variation in drainage water variables, indirect N_2O fluxes, and indirect N_2O emission factor (EF_{5g}) and mean annual indirect N_2O fluxes.

Observation period	Drainage water variable	Mean annual value	Mean seasonal value			
			Winter	Spring	Summer	Autumn
Dec, 2012−Nov, 2013	Water temperature (°C)	17.0	6.96 ± 0.62 a	21.0 ± 0.70 b	24.2 ± 0.39 b	21.4 ± 0.36 b
	N_2O flux (μg N m^{-2} h^{-1})	4.72 ± 2.85	2.13 ± 0.11 A	4.06 ± 0.71	6.80 ± 4.65	5.24 ± 3.98
Dec, 2013−Nov, 2014	NH_4^+-N (mg N L^{-1})	0.13	0.09 ± 0.02	0.07 ± 0.02	0.18 ± 0.02	0.15 ± 0.04
	NO_3^--N (mg N L^{-1})	3.17	3.53 ± 0.27 b	1.74 ± 0.15 ab	1.49 ± 0.23 a	9.32 ± 1.24 c
	DOC (mg C L^{-1})	2.17	1.31 ± 0.10 a	1.67 ± 0.32 a	3.09 ± 0.29 b	2.30 ± 0.48 ab
	Water temperature (°C)	15.3	6.50 ± 0.44 a	9.29 ± 0.58 a	23.3 ± 0.37 b	21.7 ± 0.63 b
	EF_{5g}	0.017%	0.004% a	0.006% a	0.035% b	0.004% a
	N_2O flux (μg N m^{-2} h^{-1})	5.20 ± 2.23	0.97 ± 1.10 Aa	2.51 ± 2.16 a	7.06 ± 2.52 b	7.71 ± 2.92 b
Dec, 2014− Nov, 2015	NH_4^+-N (mg N L^{-1})	0.09	0.10 ± 0.01	0.13 ± 0.06	0.10 ± 0.01	0.08 ± 0.01
	NO_3^--N (mg N L^{-1})	4.09	1.56 ± 0.29 a	1.16 ± 0.40 a	4.44 ± 1.03 ab	6.54 ± 0.17b
	DOC (mg C L^{-1})	2.30	1.50 ± 0.13 a	4.38 ± 0.68 c	2.88 ± 0.27 b	1.72 ± 0.12 ab
	Water temperature (°C)	17.6	7.74 ± 0.35 a	14.7 ± 0.81 b	23.5 ± 0.22 d	18.9 ± 0.74 c
	pH	7.56	7.68 ± 0.03	7.63 ± 0.27	7.51 ± 0.04	7.48 ± 0.07
	EF_{5g}	0.034%	0.038%	0.045%	0.039%	0.020%
	N_2O flux (μg N m^{-2} h^{-}	9.77 ± 3.99	5.78 ± 2.30 Ba	4.25 ± 1.27 a	10.02 ± 3.34 b	14.79 ± 7.00 b

Average of three years	N_2O flux (μg N m^{-2} h^{-1})	6.56 ± 1.61	2.96 ± 1.45 a	3.61 ± 0.55 a	7.96 ± 1.03 b	9.25 ± 2.86 b

Values are means ± standard errors (n = 15, 3, 15, and 2 for Winter, Spring, Summer, and Autumn, respectively, in Dec, 2012−Nov, 2013; n = 13, 4, 14, and 4 for Winter, Spring, Summer, and Autumn, respectively, in Dec, 2013−Nov, 2014; and, n = 15, 4, 23, and 17 for Winter, Spring, Summer, and Autumn, respectively, in Dec, 2014−Nov, 2015). Different lowercase letters within a row indicate differences among the seasons ($P < 0.05$), while different capital letters indicate differences among years ($P < 0.05$). Concentrations of NH_4^+, NO_3^- and DOC were measured in Dec, 2013−Nov, 2014 and Dec, 2014−Nov, 2015. Observation period for N_2O emissions in Dec, 2012−No v, 2013, Dec, 2013−Nov, 2014, and Dec, 2014−Nov, 2015 were 284, 287,and 298 days, respectively.

743 **Table 2** Comparison of EF_{5g} and indirect N_2O fluxes from drainage water,
744 groundwater and springs reported from previous studies with dominant land use type
745 of cropland.

Country	Source *	EF_{5g} (%)	N_2O fluxes ($\mu g\ N\ m^{-2}\ h^{-1}$)	Reference
		Mean (range)	Mean (range)	
UK	DW	(~0.1–1.00)[c]	/	Dowdell et al. (1979)
Japan	DW	0.20 (0.059–0.44)[b]	/	Minami and Fukushi (1984)
Japan and USA	GW	0.22 (~0.01–1.00)[c]	/	Ueda et al. (1993)
UK	GW	0.25 (0.10–0.43)[b]	0.57[a]	Mühlherr and Hiscock (1997)
	SP	0.50 (0.49–0.51)[b]	/	
USA	GW	0.13 (0.06–0.19)[c]	/	Verchot et al. (1997)
UK	GW	0.34[b]	/	Mühlherr and Hiscock (1998)
	GW	0.56[b]	/	
	GW	0.04[b]	/	
Japan	GW	0.05[c]	/	Hasegawa et al. (2000)
USA	GW	0.03[b]	0.06[a]	McMahon et al. (2000)
Japan	DW	1.27[c]	/	Sawamoto et al. (2002)
UK	GW	0.19[a]	0.85[a]	Hiscock et al. (2003)
	DW	0.01 (0.005–0.028)[d]	(~100–1000)[c]	Reay et al. (2003)
Japan	DW	0.26[c] (0.076–1.05)[a]	8.53[a]	Sawamoto et al. (2003)
UK	DW	0.20[a]	/	Reay et al. (2004a)
	DW	0.06[d]	/	Reay et al. (2004b)
Japan	GW	0.15[c]	/	Sawamoto et al. (2005)
	DW	0.18[c]	/	
	DW	0.01[c]	/	
	DW	0.05[c]	/	
Germany	DW	2.41 (0.30–4.50)[b]	/	Well et al. (2005a)
	GW	0.08 (0.002–1.58)[a]	/	Well et al. (2005b)
China	GW	0.11 (0.004–0.51)[a]	/	Xiong et al. (2006)
USA	DW	0.57 (0.01–4.07)[b]	35.2 (-8.9–266.8)[a]	Beaulieu et al. (2008)
Germany	GW	4.76 (0.007–51.0)[a]	/	Weymann et al. (2008)
	GW	0.21 (0.011–1.04)[a]	/	
	GW	0.81 (0.071–7.36)[a]	/	
	GW	2.38 (0.005–24.0)[a]	/	
USA	GW	0.22 (0.13–0.31)[a]	/	Kim et al. (2009)
	GW	0.41 (0.28–0.54)[a]	/	
UK	DW	0.30 (0.008–3.60)[a]	0.87[a]	Reay et al. (2009)
Australia	GW	2.60[b]	/	Woodward et al. (2009)
Canada	DW	0.08 (0.06–0.09)[a]	9.09[d]	Baulch et al. (2011, 2012)

Italy	GW	0.15[b]	4167[d]	Laini et al. (2011)
Ireland	GW	0.73[b]	/	Jahangir et al. (2012)
UK	DW	0.61[a]	338[a]	Outram and Hiscock (2012)
France	GW	0.12[b] (0.04–0.26)[a]	0.40[a]	Vilain et al. (2012)
Germany	GW	0.35[b]	/	Well et al. (2012)
	GW	0.20[b]	/	
Ireland	GW	0.39[a]	1.71[a]	Jahangir et al. (2013)
	GW	0.41[a]	0.80[a]	
	GW	0.30[a]	1.94[a]	
	GW	0.29[a]	2.74[a]	
USA	GW	4.40 (0.2–70.0)[a]	119[b]	Gardner et al. (2016)
USA	GW	2.07[b] (0–19.9)[a]	/	Hinshaw and Dahlgren (2016)
Sweden	DW	0.17 (0.08–0.29)[d]	127.4[b] (5.5–617)[a]	Audet et al. (2017)
UK	DW	0.12 (0.003–1.06)[a]	0.57[a]	Hama-Aziz et al. (2017)
Ireland	DW	0.06[b]	/	McAleer et al. (2017)
	DW	0.01[b]	/	
	GW	0.35[b]	/	
	GW	0.05[b]	/	
New Zealand	DW	0.01[a]	/	Premaratne et al. (2017)
China	DW	0.03 (0.004–0.19)	6.56 (-0.33–40.30)	This study
Average of the EF_{5g}		0.51[AV]	/	
IPCC default value in 2006		0.25	/	IPCC (2006)

[*] DW: drainage water; GW: groundwater; SP: spring.

[a] Data were directly provided in the original publication.

[b] Data were recalculated from those in the original publication.

[c] Data were derived from a secondary source.

[d] Approximate value.

[AV] Average of the EF_{5g} from the reference and this study (range = 0.01%–4.76%; median = 0.18%; n = 70, standard error = 0.12%, CV = 1.94).